The Synthesis and Some NMR Properties of
2,3-Bis(diphenylphosphino)-6-phenyl-λ³-phosphinine

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The synthesis, from 1,2,5-triphenylphosphole and bis(diphenylphosphino)acetylene, of 2,3-bis(diphenyl-phosphino)-6-phenyl-λ³-phosphinine, the first example of a λ³-phosphinine bearing phosphorus-containing side chains, is reported. This compound shows in its nmr spectrum the largest value of $^3J_{pp}$ (178 Hz) yet reported for a system containing the P^{III}-C-C-P^{III} linkage. Evidence is presented which supports the idea that this extraordinarily large coupling arises as a result of geometrical factors which place the non-bonding electron pairs of the two side-chain P atoms in very close proximity to one another. Reactions of the λ³-phosphinine with Ni(II) and Pt(II) compounds are briefly discussed in the context of the nmr properties of both the ligand and the complexes formed.

In an earlier publication [1], we outlined synthetic approaches to a variety of unsaturated five-membered heterocycles (for example, **1, 2** and **3**) containing both ring and side-chain phosphorus atoms, together with a brief synopsis of why such systems are both interesting and potentially useful. While some valuable synthetic procedures were developed in this study and many chemical and spectroscopic observations were made, the ultimate objective
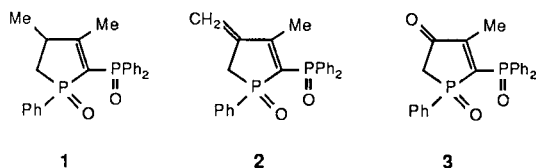

of the synthesis of fully unsaturated (and potentially aromatic) systems in which both phosphorus atoms in the P^{III} state (*e.g.* **4**) was not attained. Fully unsaturated, heterocyclic bis-phosphines similar to **4** are of particular interest to us because of their structural relationship to the well-known and versatile ligand bis(diphenylphosphino)-methane which has been the subject of much attention in our own [2] and other [3] laboratories in the formation of bis-phosphine transition metal complexes of, sometimes, quite unusual structure.

Although the methods outlined in our earlier publication [1] still have some potential for the synthesis of structures of type **4**, other recent developments in phosphorus heterocyclic chemistry suggested that it might be more productive at this time to attempt the synthesis of 2-diphenylphosphino-λ³-phosphinines (2-diphenylphosphino-λ³-phosphorins) such as the parent compound **5**. Structures of this type would be of interest in the context
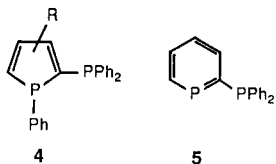
of both reactivity towards organic electrophiles and coordination studies for several reasons. For example, earlier studies of simpler λ³-phosphinines have shown [4] that the non-bonding electron pair of the ring phosphorus atom is not in the HOMO and, therefore, should be less readily available for reactions with electron acceptors. Indeed, this is normally the case since other studies [5] indicate negligible nucleophilic and basic character for these systems. On the other hand, it has been shown [6] that λ³-phosphinines will, under appropriate conditions, form σ-complexes with a variety of metal ions. This means that in reactions with organic electrophiles, probably only the side-chain phosphorus atom of **5** would be involved while with metal ions, coordination behavior in some ways similar to that observed with bis(diphenylphosphino)methane could occur. It should be noted, however, that the rigidity of the P-C-P linkage in **5** and the difference in the bite angle compared with bis(diphenylphosphino)methane, together with the 2-coordinate nature of one of the phosphorus atoms in **5**, would probably result in some interesting departures from the coordination behavior of bis-(diphenylphosphino)methane in certain circumstances. Structures such as **5**, then, should be interesting heterocycles which are also useful and unusual nucleophiles and coordinating ligands.

We report here the results of an exploratory study based upon an observation by Mathey *et al.* [7] that 1,2,5-triphenylphosphole (**6**) undergoes a thermally-induced, reversible, 1,5- shift of a phenyl group to give the 2*H*-phosphole **7**. The same group also reported [8] that similar reversible hydrogen shifts occur at much lower temperatures in simpler phospholes containing the P-H bond. Compound **7** undergoes [4 + 2] cycloadditions with a variety of alkyne derivatives under sealed-tube conditions [7] to give the bridged systems **8** and these can be made to eliminate the bridge, upon prolonged heating, to give the λ³-phosphinines **9**.
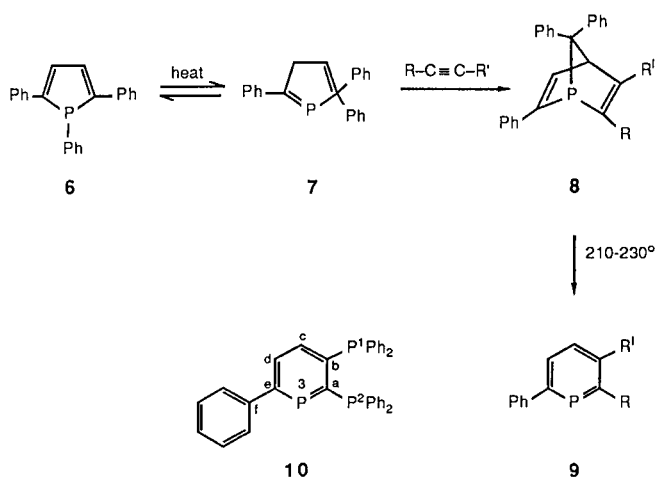
To prepare structures of type **5** using this route, the ideal situation would be one in which R = a diorgano-phosphino grouping while R' = H. There are, however, some limitations to this type of synthesis. For example, certain volatile alkynes will not react while others (such as phenylacetylene) undergo chemical changes themselves at the temperatures required for the reaction. Furthermore, alkynes in which both R and R' are bulky (as in, for example, bis(trimethylsilyl)acetylene) will not normally enter into [4 + 2] cycloadditions with **7** [7]. In any event, in such additions, the substituent orientation observed in **8** and **9** is that in which R' is the bulkier of the two substituents because of the steric crowding near the P atom in the intermediate **7**. Despite these limitations, the general feasibility of this approach to compounds similar to **5** was proven by treating the readily synthesized [9], but heavily substituted, phosphole **6** with bis(diphenylphosphino)acetylene (which also contains bulky substituents), under conditions similar to those used by Mathey *et al.* [7], to give the λ^3-phosphinine **10** which is discussed in detail below. Control of the temperature at which the reaction is carried out is of critical importance. At temperatures above 220° very tarry products are obtained while at temperatures significantly lower than this, the reaction is extremely slow and other competing reactions may take place. The probable intermediate **8** (R = R' = PPh$_2$) was not isolated from these reactions and it appears that the bridge in **8** is eliminated to give **10** at temperatures very similar to those required for the formation of **8**.

Analyses and the mass spectrum are consistent with the formation of **10** as is the ^{31}P nmr spectrum at 121.4 MHz. This exhibits a clear ABX pattern showing 12 (4 for P^3 and 8 for P^1 and P^2) of the 14 lines possible in such a spectrum. Analysis of this spectrum in the manner outlined by Becker [10] together with the generation of a simulated spectrum [11] yields the following parameters:- δ P^1 = -8.34, δ P^2 = -6.98, δ P^3 = + 228.20, $^3J_{P^1P^2}$ = 178.30 Hz, $^3J_{P^1P^3}$ = -12.38 Hz and $^2J_{P^2P^3}$ = + 19.69 Hz. The

chemical shift of P^3 is definitive for 2-coordinate phosphorus in a λ^3-phosphinine system [7,12] and the side-chain phosphorus atoms have shifts very similar to that of triphenylphosphine (δ = -6). A preliminary spectrum recorded at 32.3 MHz showed a deceptively simple pattern in which P^3 appeared as a doublet while the two side-chain P atoms appeared as a singlet superimposed upon a doublet. Only at much higher frequencies is the full ABX spectrum apparent. It should be mentioned here that the ^{31}P spectrum of **10** shows other very interesting features which are unconnected with the structural proof and which will be discussed in detail later.

Additional evidence supporting the proposed structure **10** is provided by the ^{13}C spectrum (Table I). Thus, C_a and C_e exhibit (at 75.43 MHz) signals at δ = 175.70 and 172.13 respectively which is typical [7, 12-14] of carbon atoms adjacent to the phosphorus atom in 2-substituted and 2,6-disubstituted λ^3-phosphinines. Even the α carbon atoms in λ^3-phosphinines unsubstituted at these positions show [15,16] signals as far downfield as δ = 155. The signal due to C_e is distinguished from that of C_a by the fact that it shows coupling only with P^3 and is relatively intense because of its proximity to the proton-bearing C_d. Also typical [7, 12-16] for such carbon atoms is the large value (58.2 Hz) observed for $^1J_{P^3C_e}$. A precise value for $^1J_{P^3C_a}$ could not be determined since the C_a signal appears as a weak, broad and poorly resolved multiplet as a result of coupling with all three phosphorus atoms. C_c and C_d, both of which bear hydrogen atoms, were distinguished from C_b and C_f (both quaternary) by using the DEPT [17] pulse sequence. Actual assignments of shifts for these four carbon atoms were made by comparisons with literature data [7, 13-16] for related systems and from the magnitudes of the various P-C coupling constants observed in the spectrum (Table I). The *ipso* carbon atoms of the attached diphenyl-phosphino groupings (not recorded in Table I) are observed as overlapping multiplets centered on δ = 136.95 which is virtually identical to the shift observed [18] for the

Table I

^{13}C Spectral Data for 2,3-Bis(diphenyl-phosphino)-6-phenyl-λ^3-phosphinine (**10**)

	δ	J_{P^1C} (Hz)	J_{P^2C} (Hz)	J_{P^3C} (Hz)
C_a	175.70 (m)	[a]	[a]	[a]
C_b	149.00 (m)	[a]	[a]	[a]
C_c	134.13 (ddd)	32.24 [b]	8.05 [b]	16.12 [b]
C_d	135.56 (dd)	6.04	0	12.06
C_e	172.13 (d)	0	0	58.20
C_f	142.58 (d)	0	0	26.19

[a] Unresolvable multiplet. [b] Assignments tentative (see text). [c] d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet.

ipso carbon atoms of triphenylphosphine. One point we have been unable to resolve is the unambiguous assignment of P-C coupling constants for C_c. Thus, while the value of 8.05 Hz tentatively assigned for $^3J_{P^2C_c}$ is very similar to that observed (6.7 Hz) for the *m* carbon atoms in triphenylphosphine [18,19] and the value of 16.12 Hz tentatively assigned for $^3J_{P^3C_c}$ falls in the middle of the range (13-20 Hz) previously observed [7, 13-16] for a variety of λ^3-phosphinines, 32 Hz seems large for $^2J_{P^1C_c}$ since this coupling for the corresponding *o* carbon atom in triphenylphosphine is only 19.55 Hz [18,19].

It can be seen, then, that the product obtained from the sealed-tube reaction of the phosphole **6** with bis(diphenylphosphino)acetylene has been unambiguously characterized as **10** and further interesting features of the ^{31}P spectrum of this compound will now be discussed.

The magnitude of $|^3J_{P^1P^2}|$ observed is the highest yet reported for a bis-phosphine containing the P^{III}-C-C-P^{III} linkage. These coupling constants are normally of the order 11-32 Hz for open-chain systems [20] and this holds true also for a variety of rigid phosphole dimers having structures of general type **11** [21]. In fact, the magnitude of the P^1-P^2 coupling in **10** is very similar to that observed for direct P-P coupling in biphosphines of the type R_2P-PR'_2 where coupling constants in the range 170-300 Hz are the norm [12]. It seems possible that the large value of
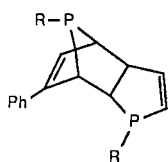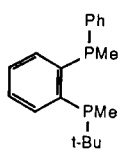
**11**   **12**
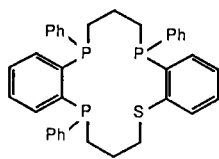
13   **14**

$|^3J_{P^1P^2}|$ observed for **10** is due in some way to the rigidly *cis*-coplanar relationship between the two side-chain phosphorus atoms and there are some data in the recent literature to support this idea. Thus, a few other structurally related bis-phosphines containing the P^{III}-C-C-P^{III} linkage have been reported to have unusually large $|^3J_{PP}|$ values. These include **12** and **13** (160 and 165 Hz, respectively) [22] and a series of bis-phosphines having the general structure **14** where three-bond coupling constants covering the range 18-146 Hz were observed [23]. In connection with this last report, it should be noted that a min-

imum value of 100 Hz has recently been established [24] for the P-P coupling in the symmetrical *cis*-1,2-bis-(diphenylphosphino)ethylene.

For the most part, little in the way of explanation has been offered for this phenomenon and some suggestions will be made here. In the only reported discussion of the phenomenon, Carty *et al.* noted that while the magnitude of the P-P coupling is largely unaffected by changes in R' and R'' in structures of type **14**, varying the substituent R apparently causes major changes. Thus, when R = *t*-butyl, $|^3J_{PP}|$ falls in the range 18-45 Hz but when R = CF_3 or Ph, values nearer 140 Hz are observed [23]. Carty *et al.* [23] attributed these variations in P-P coupling primarily to the electronic characteristics of R although it was also suggested that geometrical factors may contribute to the phenomenon. If, however, one looks at the results obtained by Carty *et al.* [23] in the light of those reported by Kyba *et al.* [22] for **12** and **13**, by Heitkamp *et al.* [24] for *cis*-1,2-bis(diphenylphosphino)ethylene and in this paper for **10**, it seems clear that three-bond P-P couplings in this wide variety of systems are uniformly high *except* when R = *t*-butyl in the series **14**. From this, one could infer that the phenomenon is almost entirely geometrical in origin and that the much lower values observed when R = *t*-butyl in the unsymmetrical *cis*-diphosphinoalkenes discussed above arise in some way from molecular distortions caused by the steric bulk of this group.

It has known for some time that in the coupling of the phosphorus atom of a tertiary phosphine grouping with a neighboring nucleus, the size of the coupling depends to a large degree on the angular relationship between the P non-bonding pair and the neighboring nucleus with coupling constants being larger when the electron pair is directed towards the neighboring nucleus. This has been well documented with P-C couplings [25]. A particularly striking example of this effect is the coupling of the tertiary phosphorus atom with the carbon atoms of the remote methyl groups in **15** where $^5J_{PC}$ has the extraordinary value of 25.9 Hz [26]. $^6J_{PH}$ is also particularly high at 5.6 Hz, while $^4J_{PP}$ was measured at 15.3 Hz. These enhanced couplings have been described in this particular case as examples of a "through space" coupling mechanism arising from steric crowding [26]. It should also be noted in passing that in phosphorus heterocyclic chemistry, several examples of unusually large (5-13 Hz) four-bond P-C couplings are known [25]. While these have been
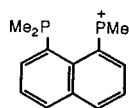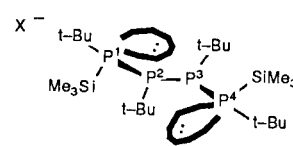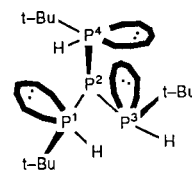
15   **16**   **17**

correlated with the direction of the non-bonding pair, the couplings have apparently not been deemed large enough to invoke "through space" effects.

Compound **10** is clearly a sterically crowded molecule with respect to the phosphorus-containing side chains. Molecular models indicate that the preferred geometry is that in which the non-bonding pair orbitals of the two side-chain phosphorus atoms are coplanar and directed towards one another with each of the diphenylphosphino groups having one phenyl group above the plane of the λ^3-phosphinine ring and one below. This has been confirmed [27] by MNDO calculations which show additionally that P^1 and P^2 have an optimum distance apart of 2.795 Å. MNDO calculations for cis-1,2-bis(diphenylphosphino)-ethylene reveal [27] a similar arrangement for the P-C-C-P skeleton but with the P atomic centers being somewhat further apart (3.194 Å).

These observations, taken with the long-range (in terms of the number of intervening bonds) P-C, P-H and P-P couplings noted [26] for **15**, indicate, therefore, that the unusually large P^1-P^2 coupling observed for **10** is a "through space" phenomenon arising from the spatial disposition of not one but two non-bonding pairs and that this is also the case for **12**, **13**, cis-1,2-bis(diphenylphosphino)ethylene and most of the related systems reported [23] by Carty et al. Further support for this view is provided by a very recent review [28] on the nmr properties of polyphosphines which discusses P-P coupling phenomena in certain saturated, open-chain polyphosphines such as **16**. The very bulky substituents on the phosphorus atoms in **16** dictate a semicircular type of geometry which directs the non-bonding pairs of the terminal phosphorus atoms (P^1 and P^4) towards one another. In such cases, $|^3J_{PP}|$ can exceed 200 Hz and this has also been attributed [28] to a lone-pair proximity effect. Similarly, a very large two-bond coupling has been observed between P^3 and P^4 in **17**. It was also noted [28] that J_{PP} in such polyphosphines increases as the following entities on the two interacting phosphorus atoms are forced into close proximity to one another:- proton-proton < proton-electron pair < electron pair-electron pair. In short, the magnitudes of P-P couplings in bis-phosphines of type **10**, **12**, **13** and **14** and polyphosphines of type **16** and **17** depend almost entirely upon the presence of *two* suitably orientated non-bonding pairs and factors such as the atoms in the backbone linking the phosphorus atoms, the length of the chain and whether or not the backbone is unsaturated have, at best, a minor influence on the coupling.

Our final, and brief, investigation in this preliminary study of the synthesis and nmr properties of **10** concerned the effect upon the three-bond coupling of protecting either or both of the non-bonding pairs of P^1 and P^2 in **10** without changing the oxidation state. Earlier work [29] on

certain mono-quaternary salts and mono-coordination complexes of cis-1,2-bis(diphenylphosphino)ethylene established that the three-bond P-P couplings shown by the non-equivalent phosphorus atoms in such systems are quite normal and in the range 18-37 Hz although it should be noted that the coupling constants for the corresponding trans- salts and complexes are even lower (7-10 Hz). The significance of this was not realized at the time because $|^3J_{PP}|$ for the symmetrical parent compound cis-1,2-bis(diphenylphosphino)ethylene was not then known to be very large. However, it appears from these observations (as would be predicted from the discussion immediately above) that both non-bonding pairs are required as free entities in these rigid, cis-bisphosphine structures if unusually large values of $|^3J_{PP}|$ are to be observed.

Attempts to confirm that this is also the case for **10** by preparing mono-quaternary salts of **10** were unsuccessful since only rather messy, uncharacterizable products were obtained. Regarding metal complexes, **10** readily forms diamagnetic cis- square-planar complexes of type **18** with both Ni(II) and Pt(II) in which both lone pairs of **10** are coordinated. The complex formed with Ni(II) shows a distorted AMX ^{31}P nmr spectrum which is readily analyzed to yield a value for $J_{P^1P^2}{}^{obs}$ of 65.9 Hz while for the corresponding Pt(II) complex, $J_{P^1P^2}{}^{obs} = 0$ Hz. Full details of these spectra are given in the Experimental. These observed coupling constants are, of course, the algebraic sum of two components - i.e. $^3J_{PP}$ through the P-C-C-P backbone and the cis- P-P coupling $^2J_{PMP}$. The contribution of $^3J_{PCCP}$ to $J_{PP}{}^{obs}$ is what needs to be established and this is not easy to do since there are relatively few model compounds in the literature. Furthermore, much depends on the relative signs of the two contributors to the observed coupling. These factors have been discussed extensively elsewhere [23,30] for other complexes although little in the way of quantitative information which can be applied to complexes of **10** has appeared in the literature. What is clear is that for **18** (M = Ni), $J_{PP}{}^{obs}$ is very similar to values of this quantity observed for the saturated chelate complexes **19** [20b] and **20** [31] in which the five-membered ring would be puckered and for which the parent phosphines have relatively small (< 35 Hz) values of $^3J_{PP}$. It is also very similar to the values observed [23] for the Ni(II) complexes of the series of bis-phosphines **14**,

18   19   20
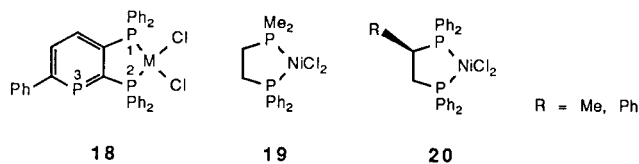
regardless of the nature of R - even when R = t-butyl. It appears, therefore, that factors such as the conformation

of th five-membered ring and the substitution pattern on the saturated or unsaturated backbone have only small effects upon the magnitude of J_{PP} observed in complexes of the type **18-20** (M = Ni). From this, it can be deduced that $^2J_{PMP}$ is the major contributor to J_{PP}^{obs} for these complexes. This becomes even clearer when the corresponding Pt(II) complexes are examined. Not only are the values of J_{PP}^{obs} very low (< 11 Hz [22] and 0 Hz in the case of **18** (M = Pt)) regardless of the nature of the backbone, they are not markedly different from values of $^2J_{PMP}$ in monodentate phosphine complexes of the type *cis*- bis(tertiary phosphine)dichloroplatinum(II) where there is no backbone contribution.

These points have been discussed to some extent, for complexes of the phosphines **14**, by Carty *et al.* [23]. However, in speculating upon why large P-P couplings in the free ligands are reduced to small backbone contributions to J_{PP}^{obs} in the spectra of chelate complexes of these ligands, Carty *et al.* attributed these changes to strain and non-planarity of the ring in the chelate complexes. In view of the foregoing discussion, this seems unlikely and we prefer the explanation advanced earlier in this paper that the large three-bond P-P couplings observed for **10** and structurally similar compounds are indeed a through-space phenomenon which requires both the presence and an optimum spatial orientation of two non-bonding electron pairs.

Further studies on the chemistry of **10** are in progress as are other synthetic approaches to simpler 2-diphenylphosphino-λ^3-phosphinines related to **5**. The results obtained from these studies will be reported in later papers.

EXPERIMENTAL

^{31}P nmr spectra were recorded at 32.3 MHz and 121.4 MHz on Bruker WP 80 and Varian XL 300 spectrometers respectively. The latter instrument was also used to record the ^{13}C spectra at 75.4 MHz. All ^{31}P and ^{13}C spectra were recorded in the proton-decoupled mode. Chemical shifts for the ^{31}P spectra were measured relative to external 85% phosphoric acid using chloroform or dichloromethane as the solvent and with deuterium oxide as the frequency lock. For the ^{13}C spectra, chemical shifts were measured relative to internal tetramethylsilane using deuteriochloroform as both solvent and frequency lock. Signals downfield of the standards are considered to be positive. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7 double focusing mass spectrometer and a direct heated inlet system. Carbon and hydrogen microanalytical data were acquired in these laboratories using a Perkin-Elmer model 240 elemental analyzer and with vanadium pentoxide used as a combustion aid. Phosphorus analyses were determined commercially by Galbraith Laboratories, Inc., Knoxville, Tennessee. Column chromatography was carried out on silica using the dry-column method. The adsorbent, specially prepared for dry column chromatography, was purchased from ICN Pharmaceuticals, Inc., K&K Laboratories Division. Melting points are uncorrected and were determined using a Gallenkamp melting point apparatus. Bis(diphenylphosphino)acetylene was purchased from Strem Chemicals, Inc., and was used without further purification.

2,3-Bis(diphenylphosphino)-6-phenyl-λ^3-phosphinine **(10)**.

1,2,5-Triphenylphosphole (1.5000 g, 4.81 mmoles), prepared by the method of Campbell *et al.* [9], and bis(diphenylphosphino)acetylene (2.4625 g, 6.41 mmoles) were intimately mixed, sealed under reduced pressure (*ca.* 10^{-7} torr) in a thick-walled, strain-free, borosilicate glass tube and heated at 220° (furnace) for 5 days. During this time, the reaction temperature was controlled to within ± 2°. The sealed tube was allowed to cool and then chilled in liquid nitrogen before opening it and crushing the brown, glass-like reaction product for easy removal. Product still adhering to the glass was removed by washing the fragments with cold chloroform (10 ml). The crude product was then heated under reflux for 3 hours in hexane to remove some of the tarry materials and the resulting suspension was chilled in a refrigerator for 12 hours prior to filtration which yielded a brown powder (2.7164 g). Recrystallization of this material from hot acetone yielded pale yellow crystals of **10** (0.4533 g, 17.5%), mp 207°; ms: M$^+$ = m/e 540; see text for ^{31}P and ^{13}C nmr spectra.

Anal. Calcd. for $C_{36}H_{27}P_3$: C, 77.78; H, 5.00; P, 17.22. Found: C, 77.58; H, 5.21; P, 16.98.

The crude material may also be purified, after the initial boiling with hexane, by dry column chromatography on silica using benzene-hexane as the eluent but the procedure described above is less time-consuming.

[2,3-Bis(diphenylphosphino)-6-phenyl-λ^3-phosphinine]dichloronickel(II) **(18, M = Ni)**.

The phosphinine **10** (0.025 g, 0.046 mmole) was treated with nickel(II) chloride hexahydrate (0.011 g, 0.046 mmole) in ethanol-chloroform (1:5, 6 ml) under nitrogen. An immediate reaction took place to give a red solution. To this solution was slowly added hexane which resulted in the formation of **18** (M = Ni) as a filterable orange solid (0.031 g, quantitative yield), mp 198° dec; ^{31}P nmr (chloroform) δ 64.86 (dd, P^2, $^3J_{P^1P^2}$ = 65.9 Hz, $^2J_{P^2P^3}$ = 37.9 Hz), 72.87 (d, P^1, $^3J_{P^1P^3}$ = 0 Hz), 228.00 (d, P^3).

Anal. Calcd. for $C_{36}H_{27}P_3Cl_2Ni$: C, 62.69; H, 4.03. Found: C, 62.20; H, 4.62.

[2,3-Bis(diphenylphosphino)-6-phenyl-λ^3-phosphinine]dichloroplatinum(II) **(18, M = Pt)**.

In a nitrogen atmosphere, the λ^3-phosphinine **10** (0.025 g, 0.046 mmole) was mixed with (1,5-cyclooctadiene)dichloroplatinum(II) (0.017 g, 0.046 mmole) in dichloromethane (5 ml). Reaction was immediate and a yellow solution was obtained. The volume of the solution was reduced to *ca.* 1 ml and hexane was slowly added. The resulting yellow precipitate was redissolved in the minimum volume of dichloromethane and, again, hexane was slowly added. The precipitate was removed by filtration and dried to give **18** (M = Pt) as a pale yellow solid (0.028 g, 67%), mp 213-214°; ^{31}P nmr (dichloromethane): δ 50.97 (P^2), 54.80 (P^1), 229.00 (P^3), $J_{P^1P^2}^{obs}$ = 0 Hz, $^2J_{P^2P^3}$ = 55.6 Hz, $^3J_{P^1P^3}$ = 0 Hz, $^1J_{P^1Pt}$ = 3664.7 Hz, $^1J_{P^2Pt}$ = 3576.7 Hz, $^3J_{P^3Pt}$ = 99.0 Hz.

Anal. Calcd. for $C_{36}H_{27}P_3Cl_2Pt$: C, 52.11; H, 3.35. Found: C, 51.99; H, 3.70.

REFERENCES AND NOTES

[1] Md. Amin, D. G. Holah, A. N. Hughes and T. Rukachaisirikul, *J. Heterocyclic Chem.*, **22**, 513 (1985).

[2] D. G. Holah, A. N. Hughes and N. I. Khan, *Can. J. Chem.*, **62**, 1016 (1984); D. J. Elliot, D. G. Holah, A. N. Hughes, S. I. Khan and S. Maciaszek, *Inorg. Chim. Acta*, **96**, L29 (1985); D. G. Holah, A. N. Hughes, H. A. Mirza and J. D. Thompson, *ibid.*, **126**, L7 (1987).

[3] For a review, see R. J. Puddephatt, *Chem. Soc. Revs.*, **12**, 99 (1983).

[4] H. Oehling, W. Schäfer and A. Schweig, *Angew. Chem., Int. Ed. Engl.,* **10**, 656 (1971); C. Batich, E. Heilbronner, V. Kornung, A. J. Ashe, III, D. T. Clark, U. T. Cobley, D. Kilcast and I. Scanlan, *J. Am. Chem. Soc.,* **95**, 928 (1973).

[5] G. Märkl, F. Lieb and A. Merz, *Angew. Chem., Int. Ed. Engl.,* **6**, 87 (1967); G. Märkl and F. Lieb, *ibid.,* **7**, 733 (1968).

[6] M. Fraser, D. G. Holah, A. N. Hughes and B. C. Hui, *J. Heterocyclic Chem.,* **9**, 1457 (1972).

[7] F. Mathey, F. Mercier, C. Charrier, J. Fischer and A. Mitschler, *J. Am. Chem. Soc.,* **103**, 4595 (1981); C. Charrier, H. Bonnard and F. Mathey, *J. Org. Chem.,* **47**, 2376 (1982).

[8] C. Charrier, H. Bonnard, G. de Lauzon and F. Mathey, *J. Am. Chem. Soc.,* **105**, 6871 (1983).

[9] I. G. M. Campbell, R. C. Cookson, M. B. Hocking and A. N. Hughes, *J. Chem. Soc.,* 2184 (1965).

[10] E. D. Becker, "High Resolution NMR, Theory and Chemical Applications", 2nd Ed, Academic Press, New York, NY, 1981.

[11] The ³¹P spectrum simulation was carried out using the PANIC Version 810515.1 program with an IBM Aspect 2000 computer. The relative signs of the coupling constants arise from the spectrum analysis and the simulation. Absolute signs for these coupling constants were not determined.

[12] L. D. Quin, "The Heterocyclic Chemistry of Phosphorus", Wiley-Interscience, New York, NY, 1981.

[13] T. Bundgaard, H. J. Jakobsen, K. Dimroth and H. H. Pohl, *Tetrahedron Letters,* 3179 (1974).

[14] F. Mathey, *Tetrahedron Letters,* 1753 (1979).

[15] A. J. Ashe III, R. R. Sharp and J. W. Tolan, *J. Am. Chem. Soc.,* **98**, 5451 (1976).

[16] G. Märkl, H. Hock and L. Merz, *Chem. Ber.,* **117**, 763 (1984).

[17] For a discussion of the DEPT procedure, see M. Bendall, D. M. Doddrell, D. T. Pegg and W. E. Hull, "High Resolution Multipulse Editing and DEPT", Bruker Analytische Messtechnik, Karlsruhe, 1983.

[18] L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, NY, 1972, spectrum No. 478.

[19] F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.,* **91**, 4940 (1969).

[20a] S. O. Grim, J. Del Gaudio, R. P. Molenda, C. A. Tolman and J. P. Jesson, *J. Am. Chem. Soc.,* **96**, 3416 (1974); S. O. Grim and R. C. Barth, *J. Organomet. Chem.,* **94**, 327 (1975); R. B. King, J. Bakos, C. D. Hoff and L. Marko, *J. Org. Chem.,* **44**, 1729 and 3095 (1979); E. P. Kyba, R. E. Davis, P. N. Juri and K. S. Shirley, *Inorg. Chem.,* **20**, 3616 (1981); [b] R. B. King and J. C. Cloyd, Jr., *Inorg. Chem.,* **14**, 1550 (1975); R. B. King, J. A. Zinich and J. C. Cloyd, Jr., *ibid.,* **14**, 1554 (1975).

[21] See, for example, L. D. Quin, K. C. Caster, J. C. Kisalus and K. A. Mesch, *J. Am. Chem. Soc.,* **106**, 7021 (1984).

[22] E. P. Kyba, C. N. Clubb, S. B. Larson, V. J. Schueler and R. E. Davis, *J. Am. Chem. Soc.,* **107**, 2141 (1985).

[23] A. J. Carty, D. K. Johnson and S. E. Jacobson, *J. Am. Chem. Soc.,* **101**, 5612 (1979).

[24] S. Heitkamp and O. Stelzer, *Inorg. Chem.,* **23**, 258 (1984).

[25] L. D. Quin in "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis", J. D. Verkade and L. D. Quin, eds, VCH Publishers, Inc, New York, NY, 1987, p 391.

[26] T. Costa and H. Schmidbaur, *Chem. Ber.,* **115**, 1374 (1982).

[27] We thank D. P. M. Lahti of the University of Massachusetts at Amherst for making available to us the results of his unpublished MNDO calculations on these systems which were carried out at our request.

[28] J. Hahn in ref [24], p 331.

[29] R. C. Taylor, R. L. Keiter and L. W. Cary, *Inorg. Chem.,* **13**, 1928 (1974).

[30] R. J. Topping and A. L. Crumbliss in ref [24], p 531.

[31] F. Morandini, G. Consiglio and O. Piccolo, *Inorg. Chim. Acta,* **57**, 15 (1982).